

REPORT No. 553

SOME EFFECTS OF ARGON AND HELIUM UPON EXPLOSIONS OF CARBON MONOXIDE AND OXYGEN

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SUMMARY

This investigation, performed at the National Bureau of Standards at the request and with the financial assistance of the National Advisory Committee for Aeronautics, is a study of the effects of the inert gases argon and helium upon flame speed and expansion ratio in exploding mixtures of CO, O₂, and H₂O. For the particular gas mixtures investigated the results show that (1) with the possible exception of He in small amounts the addition of inert gas always produces decreased flame speed and expansion ratio, (2) like volumes of A and He have very different effects upon flame speed but practically the same effect upon expansion ratio, and (3) the difference in the effect of these two gases upon flame speed is independent of the ratio of CO to O₂. A discussion of some possible modes by which inert gases may produce the observed effects is included.

INTRODUCTION

The majority of practical advances that have been made in the application of gaseous explosions to the production of useful work are of an empirical nature. So rapid have been these advances that at present our knowledge of the fundamental processes of the explosion itself lags far behind. It seems unlikely, however, that all of the possible means for improving the efficiency and performance of an internal-combustion engine will be discovered without the aid of an exact knowledge of the mechanism of the ignition and subsequent combustion of the explosive mixture within the cylinder.

It is believed that the practical value of results obtained by isolating and evaluating the effects of the individual operating variables under carefully controlled conditions will be amply demonstrated when a complete and comprehensive picture of the explosive process has been evolved. A portion of the necessary information can be obtained by the study of the effect of operating variables upon the speed with which flame transforms an explosive mixture. Experiments of this nature, using the comparatively simple fuel CO, have been in progress for some time at the National Bureau of Standards.

In reference 1 the effect of water vapor upon the speed of flame in equivalent CO-O₂ mixtures at various pressures was reported. In reference 2, means were described for improving the precision of results obtained by the soap-bubble, or constant-pressure method, developed and used by Stevens (reference 3) and data were reported showing the variation with composition of the spatial and transformation velocity of flame and of expansion ratio.

Further information upon the mechanism of the CO-O₂ reaction is presented in this report, in which the effects upon flame speed and expansion ratio of replacing a portion of the explosive mixture with the inert gases A and He are studied. These results may eventually prove of value in explaining the effects of the nitrogen that is always present in the engine cylinder.

In order to isolate the effects of the diluent gases upon flame speed and expansion ratio the present study was made at constant pressure in quiescent gas mixtures of carefully controlled composition and initial temperature. The truly inert gases A and He are better suited to the present study of the mechanism of the oxidation of CO than N₂, because it is probable that the latter is not totally inert. Carbon monoxide was selected as the fuel because it can be readily prepared in a very pure state, because it produces a highly actinic flame, and because numerous data on explosions of this fuel in the absence of diluents are already available.

A previous investigation, similar in nature to the present one, was reported by Stevens (reference 3). The subsequent study of the characteristics of the soap-bubble method (reference 2) revealed that the precision of the results could be much improved, and indicated the desirability of repeating and extending the earlier observations.

EXPERIMENTAL PROCEDURE

The method employed consists essentially in taking a photographic record on a film moving at constant speed of the travel of flame initiated by a spark at the

center of a soap bubble filled with explosive mixture. From such a record, which also contains time signals recorded simultaneously with the explosion, the spatial velocity (S_s) of flame and the final radius of the sphere of hot products (R_2) can be readily obtained. If the initial radius of the bubble (R_1) is known, the speed (S_t) with which the flame transforms the unburned gases can be calculated through the relation

$$S_t = S_s \left(\frac{R_1}{R_2} \right)^3$$

The details of the method, apparatus, and technic have been described in reference 2. The necessary connections for admitting the inert gases constituted the only significant change in the apparatus.

The A was an especially purified sample furnished by the Westinghouse Lamp Co. of Bloomfield, N. J., and specified by them to be 99 percent pure. It was used without further treatment, save drying over P_2O_5 .

The He, obtained from the Navy Department, was freed of combustibles by passage over hot CuO and of O_2 and other impurities by passage through charcoal immersed in liquid air. It also was dried with P_2O_5 before being admitted to the mixing vessel.

The bubbles were blown in a sealed chamber in which a temperature of 25° C. was maintained. The partial pressure of water vapor in this chamber was kept at 20.44 mm Hg and, by varying the composition of the soap solution, its vapor pressure at 25° C. was adjusted to as nearly this same value as was practicable. The temperature of the distilled water that was used for humidifying the gas mixtures was kept at 22.5° C., so that the partial pressure of H_2O in each of the gas mixtures was likewise 20.44 mm. Under these conditions the calculated concentration of H_2O vapor in each mixture, before the bubbles were blown, was 0.0269 ± 0.0001 mole percent and no change in the partial pressure of H_2O in the mixture should have occurred during the formation and life of the bubbles. Practically, however, it was impossible entirely to eliminate all temperature and humidity gradients in the chamber, and the resulting variations in the H_2O content of the mixtures at the time of firing are believed to account for a considerable portion of the spread in the observed results.

The first series of observations in the present study shows the effect of varying the ratio of CO to O_2 at a constant partial pressure of H_2O of 20.44 mm in the absence of inert gas. The results of this series were desired for comparison with the corresponding values of S_s previously obtained by the constant-volume method (fig. 5 of reference 2) and for reference values of S_s , R_2 , and S_t to serve as termini for the curves obtained in the presence of the inert gases. Each of the other eight series of experiments was made with the addition of measured quantities of A and He (separately) to a previously prepared mixture of CO, O_2 , and H_2O .

The method of making the mixtures was modified slightly from that given in reference 2. In order that a complete series of observations with A and with He could be made at the same ratio of CO to O_2 it was desirable to make the latter mixture in a comparatively large quantity (ca. 20 liters).

Since no provision was made for the precise determination of the temperature of the storage flasks, the direct measurement of the composition of the CO- O_2 mixtures was only approximate. More precise values of composition were obtained by measuring S_s in the absence of inert gas and reading the concentration of CO from the previously determined S_s curve, which will be presented later in figure 1. It will be shown that exact knowledge of this composition is not important so far as the comparative effect of the two inert gases is concerned. The approximate composition of each CO- O_2 mixture indicated whether it was on the rich or lean side of chemical equivalence.

Each mixture was prepared as follows. Water vapor at a pressure of 20.44 mm was admitted to the evacuated mixing vessel, and the dry mixture of CO and O_2 was then admitted to a previously chosen total pressure. Finally the inert gas was added in amount sufficient to bring the total pressure to 760 mm Hg. When a steady state was reached after each addition of gas to the mixing vessel, the pressure and temperature were observed. In order to insure complete uniformity the final mixtures (1 liter total volume) were always allowed to stand 1 hour before blowing a bubble. Each mixture consisted of enough gas for three bubble experiments, though the usual practice was to make but two observations if both appeared satisfactory.

The eight different ratios of CO to O_2 used with inert gases were distributed throughout the range of mixture ratios for which it is believed that the bubble method can be most advantageously employed. The number of observations with A was restricted by the limited available supply of this gas.

RESULTS OF THE EXPERIMENTS

The type of photographic records obtained and the method of calculating the results therefrom have already been described in reference 2. The data obtained in this way during the present investigation are most conveniently presented in graphical form.

Figure 1 shows the variation of final radius (R_2), speed of flame in space (S_s), and speed of transformation of the unburned charge (S_t) for a range of CO- O_2 mixtures containing a constant mole fraction of H_2O of 0.0269 ± 0.0001 . The square of the mole fraction of CO is plotted along the axis of abscissas to render the curves more nearly symmetrical. Each circle on the curves for R_2 and S_s represents the mean of two or more determinations. The S_t curve is derived from the other two through the relation $S_t = S_s \left(\frac{R_1}{R_2} \right)^3$, in

which the initial radius R_1 was constant throughout and equal to 4.5 cm.

The reasons for including this series of measurements have already been presented. The values of S_s given in figure 1 are directly comparable with those determined by the constant-volume method, as presented in figure 5 of reference 2. In the deviation chart (fig. 2) the mean values of S_s obtained by averaging the two sets of measurements are represented by the straight base line, while the curves show the deviations from this mean of the values of S_s obtained by the

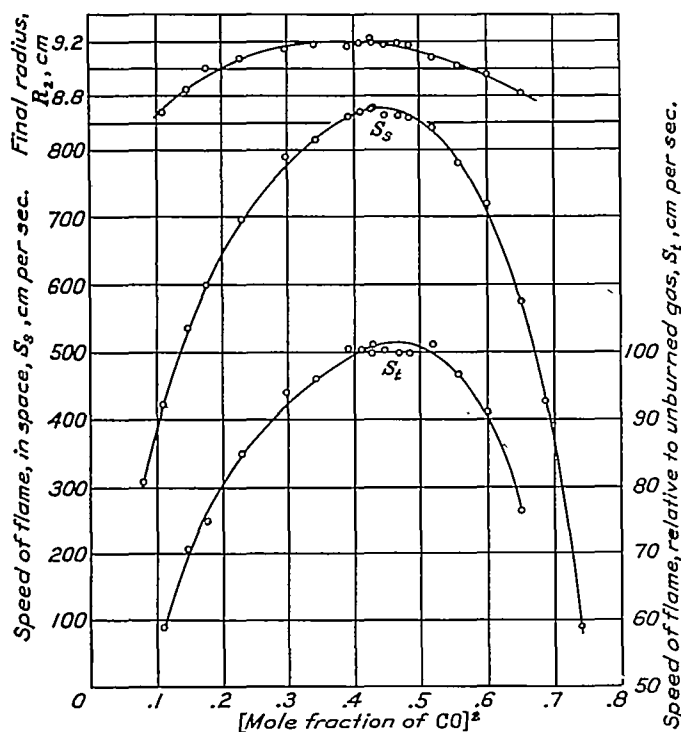


FIGURE 1.—Variation of R_2 , S_s , and S_t with the mole fraction of CO in the absence of inert gas (mole fraction of $H_2O=0.0269$).

two methods. At both the rich and lean extremes the values of S_s are changing rapidly and the personal factor involved in drawing the curves through the experimental points may be responsible for a considerable part of the deviation. The deviations in the region embracing equivalence are probably due in a large measure to failure to adjust the vapor pressure of the soap solution at 25° C. to exactly 20.44 mm. The deviation is in the direction indicating that this vapor pressure was slightly below the chosen value.

Despite this indication the differences between the values of S_s determined by the two methods seem about as small as could be expected when it is considered that an error of from 5 to 10 cm per sec. may reasonably be present in each series. It seems safe to conclude that no large systematic error occurs in one method and not in the other. Accidental errors in the reduction of the data from the photographic records are common to both methods, but their effects are greatly reduced by the fairing applied to both series of observations. It is believed that values of S_s can be determined by

either method with substantially the same precision and that at no point on either of the curves is the value of S_s in error by more than 10 cm per sec.

Some further comparisons of the data of figure 1 with those of figures 6 and 7 of reference 2 are of value in showing the effect of water vapor upon the explosive oxidation of CO. The water-vapor content in the present series of measurements was 0.0269 mole percent and in the earlier series 0.0331, while all other factors were the same for both. A change in water content from the higher to the lower of these values, no matter what the mixture ratio, always produced a decrease in S_s , an increase in R_2 , and a correspondingly large decrease in S_t . The decrease in R_2 is greatest for lean mixtures and approaches zero for very rich mixtures. The decrease in S_s is least for lean mixtures and increases gradually as the mixtures become richer. The decrease in S_t , which is of course a function of the changes in R_2 and S_s , has a minimum value near equivalence and larger values for both lean and rich mixtures. From these facts it follows that, if a mixture in a bubble at the time of firing should for some unrecognized cause contain an excess of water vapor, the observed value of S_s will be too high, of R_2 will be too low, and of S_t will be too high. These relations among the errors in the observed quantities are illustrated by several of the observations plotted in figure 1 and in the figures to be presented later in this report. The inference is that, for mixtures of CO, O_2 , and H_2O , in spite of all the precautions that have been taken to control the concentration of the latter, uncertainty in the H_2O content still remains as one of the outstanding sources of error in the results obtained by the bubble method.

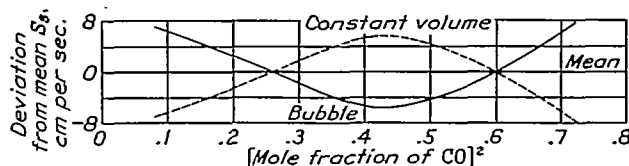


FIGURE 2.—Differences in the values of S_s observed by the constant-volume and bubble methods.

The gases A and He were selected for the present study of the effect of inert diluents for these reasons: First, it was considered that the rare gases were most likely to be inert under the conditions prevailing in an explosion; second, these two gases are the most readily obtainable of the rare gases in the desired state of purity; and, third, the heat capacities are practically identical while there is a large difference in thermal conductivity.

The data obtained in the presence of A and He for different CO/ O_2 ratios are presented in figures 3 to 10, inclusive. The same quantities (R_2 , S_s , and S_t) are plotted along the axis of ordinates as in figure 1. The mole fraction of inert gas is in each case plotted along the axis of abscissas. The crosses represent the

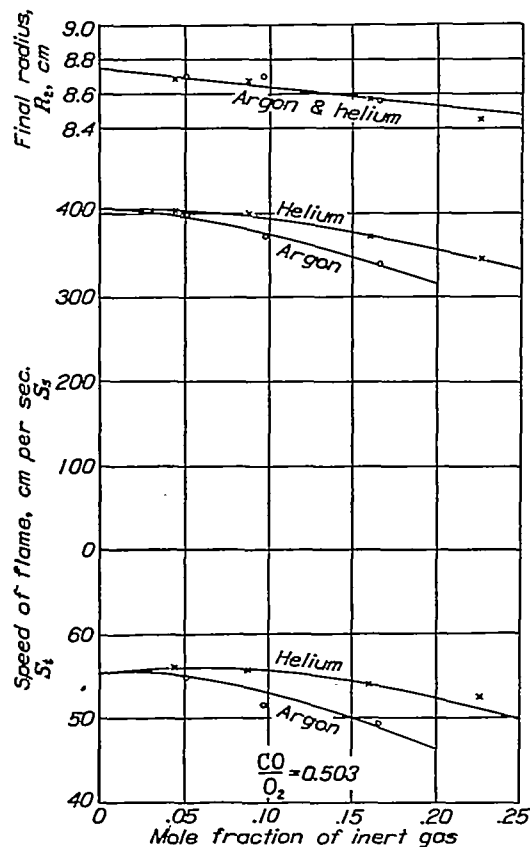


FIGURE 3.

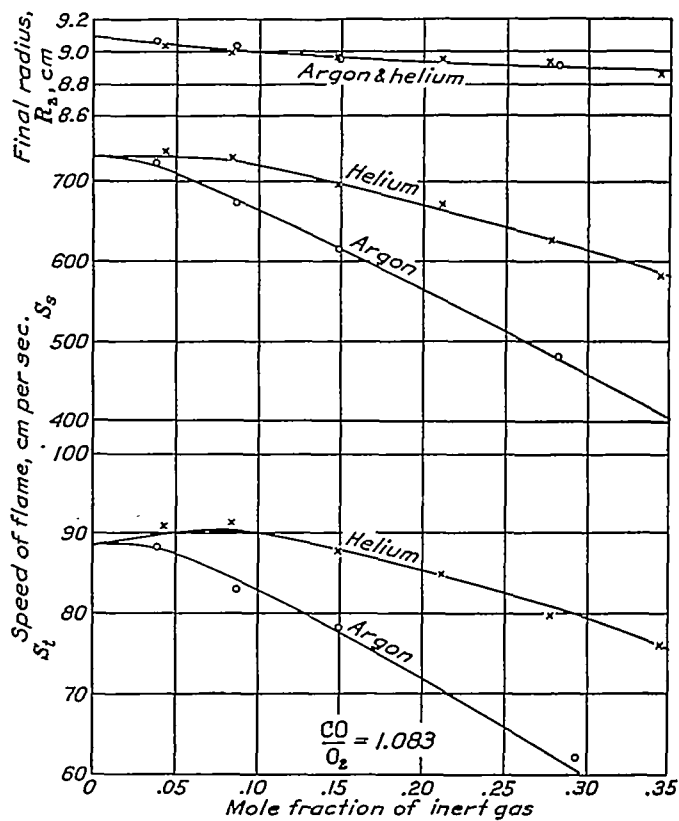


FIGURE 5.

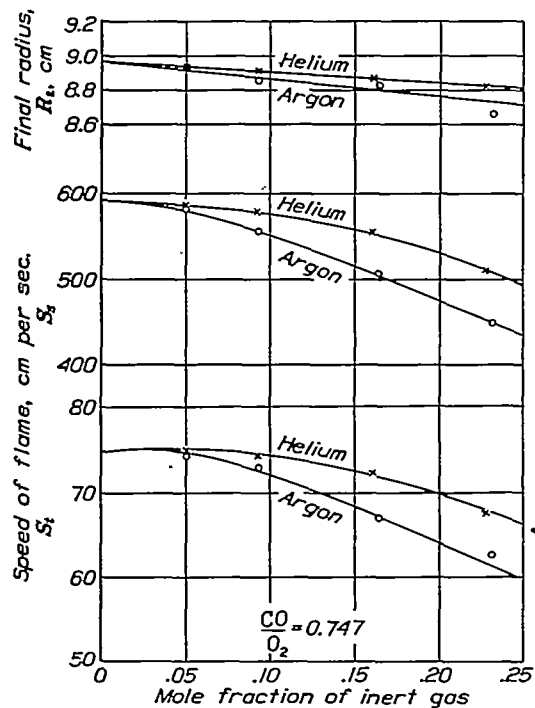


FIGURE 4.

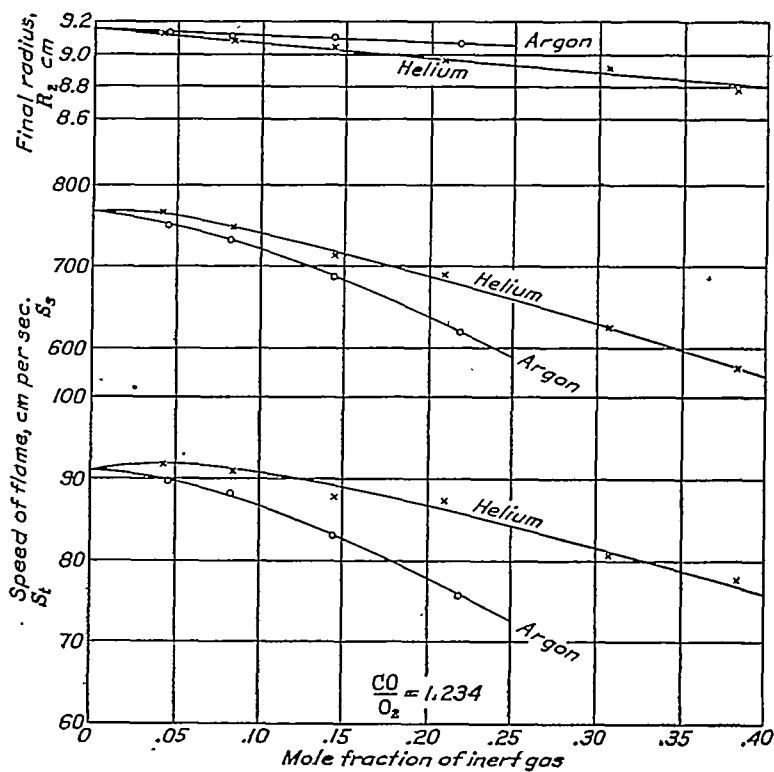


FIGURE 6.

FIGURES 3 to 6 inclusive.—Effects of argon and helium on R_f , S_f , and S_t in CO-O₂ explosions (mole fraction of H₂O=0.0269).

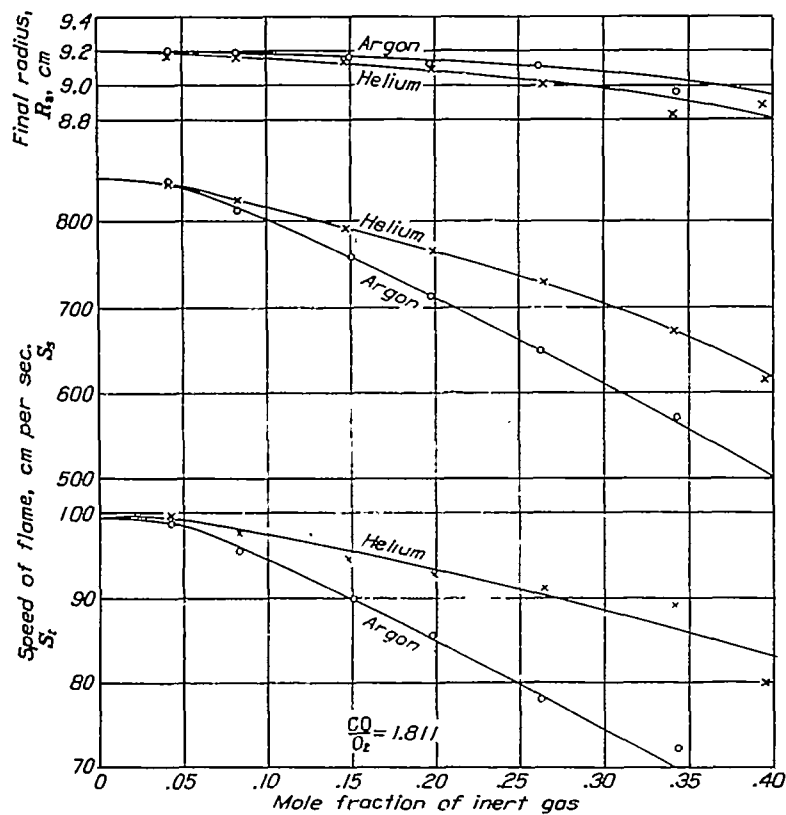


FIGURE 7.

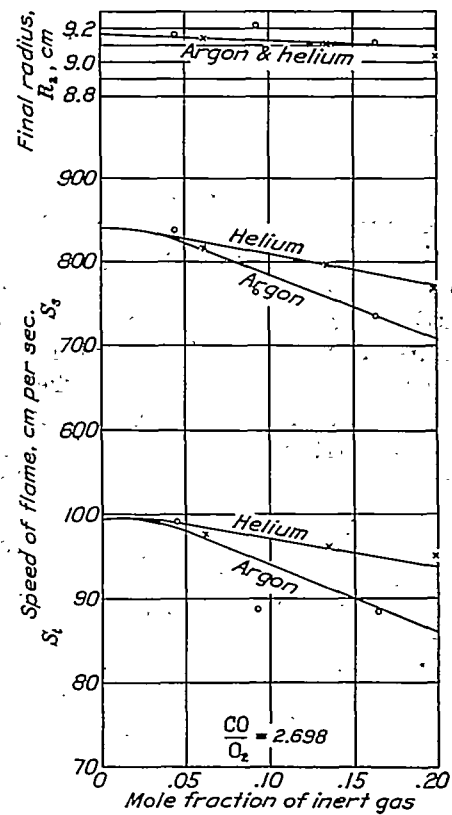


FIGURE 8.

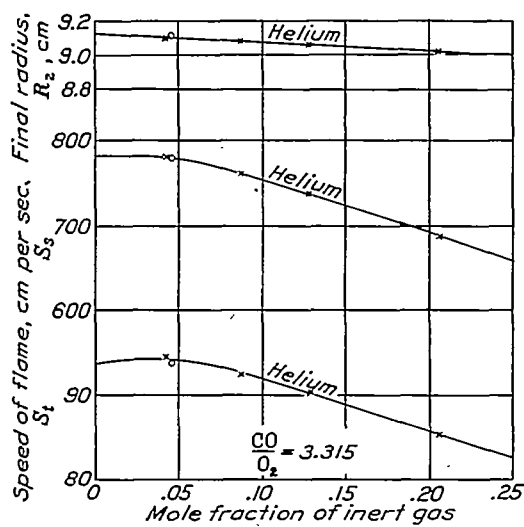


FIGURE 9.

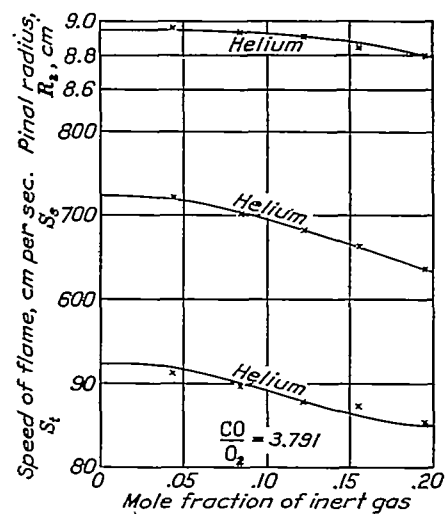


FIGURE 10.

FIGURES 7 to 10 inclusive.—Effects of argon and helium on R_2 , S_s , and S_t in $\text{CO}-\text{O}_2$ explosions (mole fraction of $\text{H}_2\text{O}=0.0269$).

experimental points for He and the open ones, those for A. Exhaustion of the A supply prevented determinations for this gas in the mixtures represented by figures 9 and 10.

ANALYSIS OF THE RESULTS

It is convenient, when analyzing the present results, to discuss separately the effects of varying the concentration of a particular inert gas and of changing from one inert gas to another.

Changes in the concentration of A or He.—In any analysis of results obtained by the present method it should be kept in mind that the total pressure and the partial pressure of H_2O were essentially constant in all the experiments and that, when inert gas was introduced, it replaced a portion of the active mixture of CO and O_2 . Therefore, an increase in the mole fraction of inert gas, as represented along the axes of abscissas in figures 3 to 10, actually involves three simultaneous and significant changes in composition: (1) A reduction in the partial pressure of CO- O_2 mixture, (2) an increase in the ratio of H_2O to active mixture, and (3) an increase in the concentration of inert gas.

The effect of each of these changes may be evaluated for the specific case of S_s in equivalent CO- O_2 mixtures, since data on the effect of pressure and concentration of H_2O vapor in such mixtures are available in reference 1. For this purpose let us consider the experiment in which 20 percent by volume of A was used. It is convenient to refer to four different mixtures, each of which represents an isolated stage in the whole process of replacing 20 volume percent of the reference mixture, in the form of CO and O_2 , with A. The characteristics of these mixtures may be tabulated as follows:

	Mixture number			
	I	II	III	IV
Total pressure (mm Hg).....	760.0	608.0	765.3	760.0
Partial pressure of H_2O (mm Hg).....	20.44	20.44	25.71	20.44
Mole fraction of CO.....	0.6487	0.6443	0.6443	0.5164
Mole fraction of O_23244	.3221	.3221	.2577
Mole fraction of H_2O0269	.0336	.0336	.0269
Mole fraction of A.....	.0000	.0000	.0000	.2000
Speed of flame in space S_s (cm per sec.).....	860	894	910	730

Mixture I is a reference mixture fired under the actual conditions of the present measurements. The value of S_s is taken from the appropriate curve in figure 1. If the total pressure of mixture I is reduced 20 percent by removal of CO and O_2 in equivalent proportions, mixture II results. The value of S_s for this mixture was obtained by interpolation of the data of figure 2 of reference 1. Mixture III is obtained by adding H_2O to mixture I until its mole fraction becomes the same as in mixture II. The value of S_s for mixture III was likewise taken from figure 2 of reference 1. Mixture IV results if A is added to mixture II in suffi-

cient quantity to restore the total pressure to the same value as that of mixture I. Mixture IV can be fired in a bubble and the value of S_s was obtained by interpolation of the present data.

The difference in S_s for mixtures III and I is $910-860=50$ cm per sec., and shows the effect of changing the ratio of H_2O to explosive mixture by an amount equivalent to that which automatically occurs when 20 percent of inert gas is added at constant total pressure and partial pressure of H_2O . The partial pressure of CO+ O_2 is the same in mixtures I and III.

The difference in S_s for mixtures II and I, $894-860=34$ cm per sec., shows the effect of simultaneous changes in partial pressure of CO+ O_2 and of the ratio of H_2O to combustible. This increase of 34 cm per sec. is thus the resultant of an increase of 50 cm per sec. due to the latter and a decrease of $50-34=16$ cm per sec., which is the effect of the pressure decrease alone.

The difference in S_s for mixtures II and IV, $894-730=164$ cm per sec., represents the true effect of the A alone, since no other differences exist in the composition of these two mixtures.

The difference in S_s for mixtures I and IV, $860-730=130$ cm per sec., is the combined effect of the three significant changes in composition that occur when 20 percent of inert gas is introduced. This decrease of 130 cm per sec. is the observed resultant of an increase of 50 cm per sec. due to the increase in the ratio of H_2O to explosive mixture, a decrease of 16 cm per sec. due to the reduction in the partial pressure of the CO+ O_2 , and a decrease of 164 cm per sec. due to the A.

As already shown, the true effect of introducing 20 percent of A is a decrease in S_s of 164 cm per sec., while the observed effect of the three simultaneous changes in composition is only 130 cm per sec. Similar calculations for other concentrations of both A and He show that this same order is always maintained in equivalent mixtures of CO and O_2 . Quantitative data for mixtures of CO and O_2 in other proportions are not available, but it has been shown that, qualitatively, the effect of water vapor is in the same direction for all ratios of CO to O_2 as at equivalence. It is therefore concluded that, if curves showing the effect upon S_s of the inert gases alone could be obtained, they would lie below the S_s curves of figures 3 to 10 at all points except those for zero concentration of inert gas, and that the separation would increase with the concentration of inert gas.

Unfortunately sufficient reliable data to permit a similar isolation of the effects of inert gases upon R_2 and S_s do not exist. A qualitative estimate is possible, however, for it has been shown that in the range of concentration of water vapor here involved, an increase in the mole fraction of H_2O always produces a decrease in R_2 . This is probably a direct result of the increase in the amount of heat retained by the H_2O

as kinetic energy. Nothing very definite can be said about the effect of pressure upon R_2 for want of reliable experimental results. Some decrease in the volume of hot products is to be expected when the initial pressure is reduced at a constant mole fraction of H_2O because of the greater dissociation of CO_2 at lower pressures. The changes in R_2 resulting from the addition of inert gas as displayed in figures 3 to 10 are therefore the resultant of the three decreases due to the increase in the ratio of H_2O to unburned gas, to the decrease in partial pressure of the active mixture and consequent less complete oxidation of the CO , and to the presence of the inert gas. The effect of the latter alone would therefore be expected to be less than is shown in the figures.

If the curves given for R_2 are too low and those for S_i too high, it follows that those for S_f are also too high.

It is concluded that when the effects of inert gases upon flame speed and expansion ratio are investigated by a method in which it is practicable to eliminate the effect of varying the initial partial pressure of the unburned gas and the ratio of H_2O to unburned mixture, it will be found that A and He actually produce less decrease in R_2 and greater decreases in S_i and S_f than are shown in the figures.

Differences in the effects of A and He.—In contrast with the rather obscure effect of the change in concentration of inert gas, the differences in the effects produced by like volumes of A and He can be obtained directly from the figures, since the substitution of one inert gas for the other involves no further change in the initial composition of the mixture.

It will be noted that in figures 6 and 7 the values of final radius (R_2) seem slightly higher for A; in figure 4 the He gave the higher values, and in figures 3, 5, and 8 the effect of these two gases on R_2 seems to be identical. In those cases where differences are shown they are of an order of magnitude comparable with the error that may reasonably be expected in the observed values of R_2 . Therefore the present measurements should not be considered sufficiently precise to show definitely that like volumes of A and He may produce different changes in final radius. If real differences actually exist, the present results show that they are very small and, for the purpose of the following discussion, it is necessary to consider only one of the flame speeds (either S_i or S_f) since these are exactly proportional for identical values of R_2 .

Slight increases in S_i at low concentrations of He are shown in some of the figures. These increases are of a magnitude comparable with the experimental error and may or may not be significant.

It is evident in each of figures 3 to 8 that a given volume of He offers less hindrance to the progress of the reaction zone than a like volume of A. From each of these figures a series of differences in S_i , when like volumes of He and A are present, may be

read off at arbitrarily chosen values of the mole fraction of inert gas. An assembly of such data is presented in figure 11. The horizontal dashes represent the individual differences and the dots the means of these differences. Each horizontal dash in any vertical line thus represents the difference in S_i for mixtures containing corresponding amounts of He and A at a chosen ratio of CO to O_2 . The order of the departure of the dashes from the mean does not show

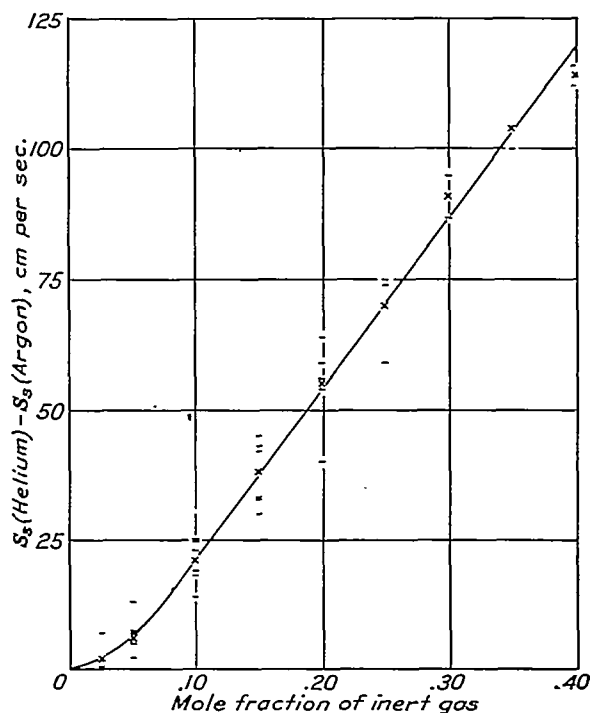


FIGURE 11.—Differences in the effect upon S_i of argon and helium for all ratios of CO to O_2 .

any systematic relation to mixture ratio. In addition, the ordinates of the dashes are differences between two quantities to each of which a tentative tolerance of ± 10 cm per sec. has been assigned. For these reasons the spread of the dashes is believed to be no greater than the experimental error and the curve that has been fitted to the dots is considered a satisfactory representation of the present results.

From this curve it is concluded that, within the limits of error of these experiments, the difference in the effect of A and He upon flame speed is independent of the ratio of CO to O_2 and that this difference increases linearly with the concentration of the inert above 7 percent. No logical explanation for the curvature at low concentrations of inert gas has been found. The curve must pass through the origin, but no straight line through this point represents the data satisfactorily.

The problem of explaining the observed differences in the effects of A and He is difficult because we do not know the mechanism of the action of either. We do know that with the possible exception of He in small amounts, both reduce flame speed, that identical vol-

umes retain virtually the same fraction of the total chemical energy liberated by the oxidation of the fuel, and that at room temperature the specific thermal conductivity of He is over 8 times that of A. This last fact, together with the rather natural supposition that the ability of gases to conduct heat is important in fixing the speed at which flame travels through an explosive mixture, seems to offer at once a qualitative explanation of the present results. Before such an explanation is accepted, however, it may be well to see how it agrees with other known facts.

It was predicted by the kinetic theory of gases, and has since been experimentally verified, that the thermal conductivity, viscosity, and diffusivity of a gas are related properties, since each is intimately connected with the mean free path of the molecules. The question at once arises as to why the thermal conductivity has been selected as the one of these four properties most significant in the propagation of flame. One reason may be that, by its use, an easily visualized physical picture has been evolved by numerous authors, on the assumption that heat is conducted from the flame to the active gas where inflammation occurs when the so-called ignition temperature is reached. Lewis and von Elbe (reference 4) give numerous citations to such theoretical treatments. Although the simplicity of such a picture is very appealing, it does not seem to be in complete accord with other related ideas or with various experimental results in the field.

In the first place it would seem that if this picture were correct, greater theoretical advances would have been made since its initial appearance more than 40 years ago. In spite of the fact that the velocity of an average molecule is high compared with normal flame velocities, the actual rate of resultant displacement of such a molecule is much less than the rate of propagation of flame. Stated in other words, the interdiffusion of gases is a comparatively slow process. These facts suggest that the commonly pictured process of conduction of heat in a gas is too slow to have much influence upon flame speed.

As pointed out by Lewis and von Elbe (reference 4) there is considerable evidence that inflammation of an active mixture can be produced at temperatures much below the ignition temperature by the introduction of a comparatively small number of active particles. If such particles are produced in the flame it seems logical to suppose that some of them will advance into the unburned charge at a faster rate than the flame itself. Physically, then, the chief difference between the mechanism proposed by Lewis and von Elbe and that involving the idea of thermal conduction is one of degree, the former requiring the advance of a much smaller number of particles ahead of the reaction zone than the latter. In spite of the fact that the conduction of heat and the interdiffusion of gases are comparatively slow processes, it is not difficult to conceive that a

relatively small number of particles from the flame are at all times advancing through the flame front and into the unburned gas ahead of it. Such action may result from the fact that some of the particles are moving at velocities far in excess of the average, or that, even though all the particles capable of producing activation were possessed of the same velocity, through sheer chance some of them would move farther than others before suffering collision or loss of the power of activation.

From the material that has been presented there seems to be some reason to suppose that the rate of flame propagation should depend to a considerable extent upon the free paths of some of the particles borne in the flame and that the free paths of particular interest are far in excess of the average or mean free path of all members of the species.

Regardless of the mechanism by which flame propagates, the replacement of active mixture with inert gas, as was done in the present measurements, may be thought of as the introduction of a resistance, in the form of intermediate collisions, to the transfer of energy in some form from the flame to the unburned gas. The magnitude of the resistance depends upon characteristics of the inert gas that have not yet been definitely identified. Some reasons for and against the selection of thermal conductivity have already been stated. On the basis of the activation theory of Lewis and von Elbe (reference 4) the explanation of the observed differences in the effects of A and He is possibly not quite so obvious.

In the first place, it is impossible to calculate the rate of diffusion of any species from the flame into the mixture of gases ahead of the flame front. We do know, however, that the mean free path of He is approximately three times that of A and that gases therefore diffuse more rapidly through He. In other words, it would be expected that with identical conditions both as to concentration and average translational energy prevailing in the flame, a greater number of particles from the flame would advance per unit time into an unburned charge containing He than into one containing the same volume concentration of A. This being the case it seems logical that flame should progress more rapidly in the mixtures containing the He. Furthermore, once a molecule of unburned gas has received the necessary energy from the flame to cause it to react upon the next collision with its complement molecule, it must first diffuse through the comparatively cold gases until the complement molecule is found. The presence of He would offer less resistance to this process than the presence of a like volume of A.

It may be well to point out also that if activation is electrical in nature, that is, if it is accomplished by reason of charges borne by the activators, the mass absorption coefficient of A for electrons and for positive

ions is greater than that of He, so that the charged particles would have a greater probability of reaching the unburned charge before losing their activity in the presence of He.

If it be true that the two rates of diffusion, namely, (1) that of active particles from the flame into the unburned charge and (2) that of the activated molecules through the charge to their complement molecules, are primarily responsible for fixing the speed of flame relative to the unburned gases, then it is to be expected that the heat capacity of the diluent gas will have little or no effect upon this speed. Such an expectation would not be fulfilled if it were found that the probability of an activator losing its potency upon collision with a molecule of inert gas varied with the nature of the inert gas. The heat capacity of the inert gas will, however, be important in fixing the final temperature attained by the products of combustion, and by this means it will influence expansion ratio and the speed of flame in space.

COMPARISON WITH THE RESULTS OF STEVENS

The present measurements are essentially a repetition and extension of those which Stevens (reference 1) made by the same method. The results of the two series, however, disagree even qualitatively. It has already been pointed out in reference 2 that in the earlier measurements the control of the water-vapor content of the bubbles at the time of firing was inadequate for explosions of CO. This fact alone will hardly account for the difference in results shown by the two series of measurements, because Stevens concluded that "argon has practically the same effect on the rate of propagation of the reaction zone in the CO-O₂ explosive reaction as the inert gas helium." In addition, his values for the transformation velocity S_t in mixtures containing 40 percent of CO or less are higher than those which he obtained in the absence of inert gas. This latter result is not only at wide variance with the present data, which show that a decrease in S_t results upon addition of both A and He regardless of the ratio of CO to O₂, but is also quite difficult to explain.

It is likewise very difficult to find a logical reason for the fact that his observed results vary as they do from the present results. The deviation is particularly noticeable for his results in the presence of A. Both the A and the He used in the present measurements were taken from cylinders procured by Stevens and it is probable that the gases which he used came from these same cylinders. In a few experiments with lean mixtures the He was used directly from the cylinder without purification, and an increase in flame speed was observed up to a certain concentration of impure He. This result indicates the presence of combustible material that burns more rapidly than CO. The presence of such materials in the He during Stevens'

measurements might account for a portion of the increase in flame speed in his lean mixtures containing this inert gas. As has been stated, these impurities were removed in the present experiments by passage over hot copper oxide and then charcoal immersed in liquid air.

The A, however, was used in both series without purification, except the passage over P₂O₅ in the present experiments. It is highly improbable that the A contains any impurities besides other members of the rare gas group and atmospheric air. None of these could conceivably produce the high values of flame speed observed by Stevens, this contention being amply verified by the present measurements. No satisfactory explanation has been found for the high values he obtained with A or for the identity of his values for A and He.

Since it is certain that large errors exist in the earlier measurements with A and He and since it is known, both from the results reported in reference 2 and those here presented, that an equation of the type $S_t = K_1[\text{CO}]^a[\text{O}_2]$ is inadequate to represent the more precise results in the absence of inert gas, it is futile to modify an equation of this type by an additive term to take into account the effect of inert gases. Stevens' equation

$$S_t = K_1[\text{CO}]^a[1 - \text{CO}]^{\alpha + \beta G_i}$$

in which K_1 , a , and β are empirical constants, and G_i is the concentration of the inert gas, is therefore untrustworthy and the values of the constants K_1 and β found by Stevens are very different from those indicated by the more precise results. In fact, no constant values of K_1 and β , when substituted in the above equation, give an adequate representation of the present results.

CONCLUSIONS

The following conclusions are drawn from the results that have been presented.

1. The earlier belief (reference 2) that satisfactory agreement existed between values of S_t determined by the constant-volume and bubble methods has been confirmed over the entire range of mixture ratios.
2. Previous results (reference 1) indicated that an increase in the concentration of water vapor up to saturation at room temperature always produced an increase in the spatial velocity of flame in equivalent mixtures of CO and O₂. A comparison of the present results with those of reference 2 shows that this statement may be extended to include all values of mixture ratio, and that increasing the H₂O content of any mixture (up to saturation at least 25° C.) likewise results in decreased values of R_2 and increased values of S_t . The magnitude of these changes varies somewhat with mixture ratio.
3. The substitution of A or He for active mixture always produces a decrease in R_2 . Like quantities of

these inert gases have almost, if not exactly, the same effect upon R_2 .

4. Argon always produces a greater decrease in flame speed, both in space (S_s) and relative to the active gas (S_r), than does a like volume of helium.

5. Simultaneous changes in the concentration of H_2O and inert gas are inherent in the bubble method. It is shown that when the effects of the former are eliminated the values of R_2 become higher and those of S_s and S_r become lower than those shown in figures 3 to 10. In other words, the effects of A and He alone upon flame speed are actually somewhat greater than is shown in the graphs, while the effect upon expansion ratio is less.

6. The difference in the effect of A and He, which is shown directly in the present results, is independent of the ratio of fuel to oxygen.

7. This difference is a linear function of the concentration of inert gas above 7 percent. No explanation has been found for the different shape of this function at low concentrations of inert gas.

8. It is believed that the heat capacity of the inert gas influences the expansion ratio, and through it the spatial velocity of flame, but is of little or no importance in fixing the velocity of transformation of the active gases.

9. It is also believed that the free path of the molecules of an inert gas, which governs the rate at which other particles diffuse through it, is of primary impor-

tance in determining the effect of the inert gas upon the transformation velocity.

10. The present results disagree with previous measurements made by Stevens (reference 3) using the same method. The differences may be assigned in part to the inadequacy of the control of the concentration of water vapor in his experiments. Impurities in the He used by Stevens may have been responsible for a portion of the increase in flame speed which he observed upon addition of this gas to lean mixtures. For A, however, the cause of the difference still remains obscure.

NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C., *September 25, 1935.*

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